

## STATISTICAL EVALUATION OF PHYSICAL PROPERTIES FOR COAL MACROMOLECULES BASED ON COMPUTER-GENERATED STRUCTURES

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### INTRODUCTION

Computer-Aided Molecular Design (CAMD) has recently been introduced in the area of coal science (1-6). Carlson and co-workers (1) used CAMD to model in three dimensions previously published coal structures. The structures were submitted to molecular mechanics and dynamics. The potential energy, the true density, and the microporosity were evaluated for each model (2). Nomura and co-workers have also used CAMD to study their own coal model (3). Using molecular dynamics with periodic boundary conditions, Murata (4) correlated potential energy and true density. An important point needs to be mentioned regarding the utilization of CAMD for the study of coal; prior to use of CAMD software, the connectivity (i.e. the structural formula) of the studied molecule has to be known. This information is unfortunately lacking for coal.

Many studies (7) have been conducted in the past 25 years to resolve by computer the general problem of retrieving a structure from analytical data. The generic name for these studies is Computer-Aided Structure Elucidation (CASE). We recently developed a new CASE technique (the SIGNATURE program ref. 8) for the modeling of complex macromolecules. The technique is able to construct large molecular models from analytical structural data and has already been applied to devise models for vitrinite maceral from HvC bituminous coal (5,6). Aside from constructing models in three-dimensional space, the SIGNATURE program is also able to compute the number of models possible (7). Knowledge of this number is crucial to our being able to decide how many models are necessary to represent coal. Even if this number is too large to allow all the models to be built, sampling theory makes it possible to select a subset of models (a sample) which is statistically representative of the whole population (9). Among the various techniques of sample design, the Simple Random Sampling Without Replacement (SRSWOR ref. 9) is the most convenient to apply here. The SIGNATURE program can directly build the required sample because the program permits the construction of non-identical random models.

### METHOD

The experimental material chosen for this study was a piece of coalified wood, specifically a fossil stem which was recovered from a lacustrine shale from the Midland Formation (Triassic) near Culpoper, Virginia. In a previous report (10), we assumed that this coalified wood is representative of vitrinite from HvC bituminous coal. The analytical data supplied to the SIGNATURE program (published earlier, ref. 10) are summarized in Table I. The SIGNATURE program was run and all the solutions containing 333 carbon atoms were searched. This number of carbons was chosen considering the computational time and the fact that all the fragments listed in Table I must be present in the models. The SIGNATURE program found only five different molecular formulas (Table II) having a deviation between model and analytical data less than 1%.

As presented in Table II, the population of possible coal models is subdivided into five different C<sub>333</sub> structures. To build a sample which is a good representation of the entire population, the sample size of each C<sub>333</sub> structure has to be proportional to the corresponding population of all of its possible isomers. Considering the population size of each C<sub>333</sub> structures (Table II) and the computational time required to build the structures and evaluate the different

characteristics, we chose to build a sample of  $n_1 = 15$  structures comprising the following: 2 structures of  $C_{333}H_{302}O_{16}$ , 10 structures of  $C_{333}H_{304}O_{16}$ , 1 structure of  $C_{333}H_{306}O_{16}$ , 1 structure of  $C_{333}H_{308}O_{16}$ , and 1 structure of  $C_{333}H_{310}O_{16}$ . For each of the 15 models, minimum energy conformations were calculated using a procedure described in a previous report (5). Then, physical characteristics were evaluated using a program initially devised to compute the physical true density (2,5), and updated to determine the micropore volume (6). In the present paper, the program was extended in order to compute the surface area. Briefly, the surface area is computed by immersing the molecular model in a grid composed of cubic cells of length  $r$  (generally  $r = 1 \text{ \AA}$ ). We define two types of surface area - the total surface area, and the pore surface area. The total surface area represents the actual surface of the structure. This surface is computed by summing all the areas of cell faces tangent to the Van der Waals sphere of an atom. The pore surface area is the surface of the micropore volume. The pore surface is computed by summing of the areas of cell faces which belong to a micropore cell (i.e. a cell located inside a micropore) and are tangent to the Van der Waals sphere of an atom.

The results for the physical characteristics are presented in Fig. 1. Means and variances were calculated using the SWRSOR procedure developed by Cochran (9).

## DISCUSSION

All 15 of the constructed  $C_{333}$  models agree well with the quantitative analytical data with an average deviation of less than one percent. The number of cross-links varies between 2.5 and 5 for each  $C_{333}$  structure, and the molecular weight per cross-link averages 1205 amu with a standard deviation of 254 amu. This value agrees well with swelling experiments for acetylated and pyridine extracted bituminous coal, where the molecular weight per covalent cross-link ranges between 900 and 1500 amu (11). Furthermore, the average number of aromatic fragments between cross-links (7.9) is in the range of values obtained from swelling experiments (4-8 aromatic fragments between cross-links ref. 11,12).

Fig. 1 shows that the potential energy increases slightly with the number of cross-links (1.85 kcal/atom for the model having 2.5 cross-links and 2.14 - 2.16 kcal/atom for the two models having 5 cross-links). However, overall, the energy values are clustered, and as a direct consequence, the variance is small (Fig. 1). Another interesting point was observed when the structures were depicted on the computer monitor. Independent of the cross-link density, the global conformations appeared very similar. This suggests that even when the structures are not highly covalently cross-linked, they are held together by van der Waals interactions. A related observation is that no major changes in helium density and porosity were observed for the models investigated containing different cross-link densities (Fig. 1).

The computed helium density averages 1.26 g/cc for all 15  $C_{333}$  structures constructed with the population deviation being less than 2 percent. This result is in good agreement with experimental results found for vitrinite at a rank of bituminous coal (1.25 - 1.30 g/cc, ref. 13). The computed micropore volume averages 0.030 cc/g with a population deviation of 13 percent. The micropore volume is slightly lower than experimental values found for coals of HvC bituminous rank (0.039 - 0.070 cc/g, ref. 14). The low microporosity may be due to the size of our models; they are very small compared to the particle sizes used in porosimetry experiments.

The calculated total surface area for all of the 15 models averages  $3693 \pm 29 \text{ m}^2/\text{g}$ . This is at least 10 times larger than the values measured by  $\text{CO}_2$  absorption, and about 100 times larger than the BET surface area obtained with  $\text{N}_2$  for the same rank of coal (15). However, the calculated total surface area cannot be correlated with experimental results because the sizes of our models are small, and the external surfaces (surfaces of the boundaries of the structures) are much larger than the internal surfaces (surfaces of the micropores). This contrasts with experimental results, where the external surface area is negligible compared to the internal surface area (15).

Since the micropore surface area is dominant experimentally, we should expect our pore surface calculation to be in better agreement with experimental results. We find the micropore surface area calculated for our models is relatively close to the  $\text{CO}_2$  surface area measured for HvC

bituminous coal (120-250 m<sup>2</sup>/g, ref. 15). Our mean value (292 m<sup>2</sup>/g) is slightly larger than experimental values, probably due to our calculation method. Our method for surface calculations uses a cell grid size of 1 Å length. The same calculations made with a doubled grid size (2 Å) for the first C<sub>333</sub> structure of the sample (C<sub>333</sub>H<sub>302</sub>O<sub>16</sub>) gives a micropore surface area of 190 m<sup>2</sup>/g. It is known that the surface area of coal behaves like a fractal surface (16-19); therefore, an increase in the cell size leads to a decrease in the surface area. Fig. 2 correlates on a log-log scale different sizes of the cell grid and the number of cells which belong to the pore surface for the structure C<sub>333</sub>H<sub>302</sub>O<sub>16</sub>. According to Pfeifer and Avnir (20), the negative slope of the line is the fractal dimension (D = 2.68 in the example of Fig. 2). The fractal dimension of the total surface area was also calculated for each of the C<sub>333</sub> models comprising the sample using a cell grid size varying between 1 Å and 8 Å (Fig. 3). Using the SRSWOR technique, the mean value found was D = 2.71 and the population deviation found was only 0.05.

In summary, we have been able to develop a technique that uses the power of the computer to create a number of molecular models for coal using actual quantitative and qualitative experimental data, and to show that the models, from a statistical viewpoint, are a good representation of the coal structure. Previous attempts to elucidate the molecular structure of coal, including previous computer models, necessarily included investigator bias and could not be proven to be representative or average coal structures. In the present study, we can conclude that for the physical properties investigated, a sample of 15 structures is sufficient to represent statistically the whole population of vitrinite from HvC bituminous.

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**Table I.** Analytical data for HvC Bituminous coalified wood (Midland Stem, ref. 10).

Parameter	Analytical Data	Model (C <sub>333</sub> H <sub>302</sub> O <sub>16</sub> )	Deviation Analytical data - Model
<b>Elemental analysis and carbon-13 NMR data (normalized for 100 carbon atoms)</b>			
C	100.0	100.0	-
H	92.0	91.8	0.2
O	5.0	4.6	0.4
f <sub>a</sub> (aromatic carbon)	62.5	63.0	-0.5
f <sub>a</sub> <sup>H</sup> (protonated aromatic carbon)	28.0	27.6	0.4
f <sub>a</sub> <sup>P</sup> (phenolic or phenolic ether)	7.5	7.5	0.0
f <sub>al</sub> (aliphatic carbon)	37.5	37.4	0.1
f <sub>al</sub> <sup>H</sup> (aliphatic CH or CH <sub>2</sub> )	26.0	26.2	-0.2
f <sub>al</sub> <sup>*</sup> (aliphatic CH <sub>3</sub> )	11.5	11.2	0.3
Average deviation			± 0.26
<b>Flash Pyrolysis/gc/ms data (weight % normalized to total aromatic fragments)</b>			
benzene	3.3	2.0 (1)	1.3
toluene	4.8	4.8 (2)	0.0
C-2 benzenes	5.2	8.3 (3)	-3.1
C-3 benzenes	3.9	6.3 (2)	-2.4
phenol	3.6	2.5 (1)	1.1
<i>o</i> -cresol	5.7	2.8 (1)	2.9
<i>m</i> + <i>p</i> -cresol	13.0	8.5 (3)	4.5
2,4 dimethylphenol	12.0	9.6 (3)	2.4
other C-2 phenols	10.3	6.4 (2)	3.9
C-3 phenols	10.9	14.2 (4)	-3.3
C-4 phenols	4.8	3.9 (1)	0.9
alkylnaphthalenes	17.0	24.4 (6)	-7.4
alkyldibenzofurans	5.2	6.2 (1)	-1.0
methyl	-	(7)	
ethyl	-	(9)	
propyl	-	(3)	
C4-C22	-	(0)	

Values in parentheses are the quantities of each fragment corresponding to a molecule containing 333 carbon atoms.

**Table II.** Deviation analytical data - model and population information for each of the C<sub>333</sub> molecular formula<sup>a</sup>

Molecular Formula	Average deviation <sup>b</sup>	Number of possible models
C <sub>333</sub> H <sub>302</sub> O <sub>16</sub>	0.26	52,272
C <sub>333</sub> H <sub>304</sub> O <sub>16</sub>	0.29	231,000
C <sub>333</sub> H <sub>306</sub> O <sub>16</sub>	0.39	24,750
C <sub>333</sub> H <sub>308</sub> O <sub>16</sub>	0.49	9,856
C <sub>333</sub> H <sub>310</sub> O <sub>16</sub>	0.71	1,440

<sup>a</sup> The numbers of possible models have been estimated using the isomer generator provided by the SIGNATURE program (8). <sup>b</sup> The deviation is the average deviation between model and quantitative analytical data as calculated in Table I.

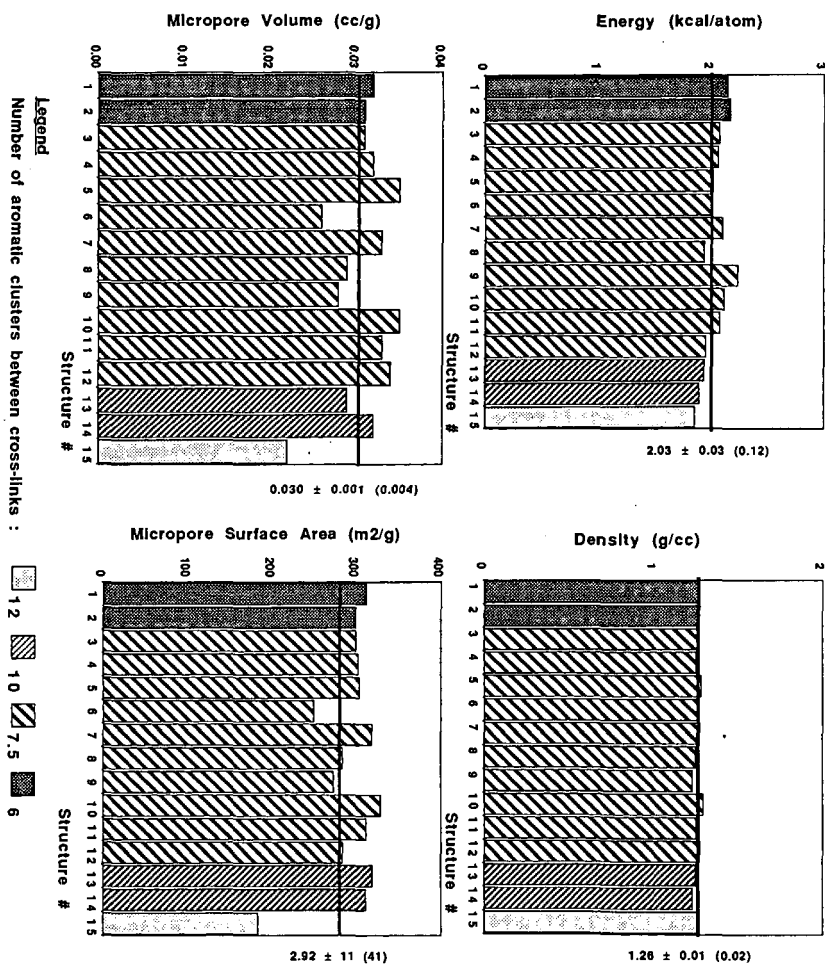


Fig.1. Correlation between physical characteristics and cross-link densities for each of the 15 individual models comprising the sample. For each graph, the horizontal line represents the population mean. The population deviations are indicated in parentheses.

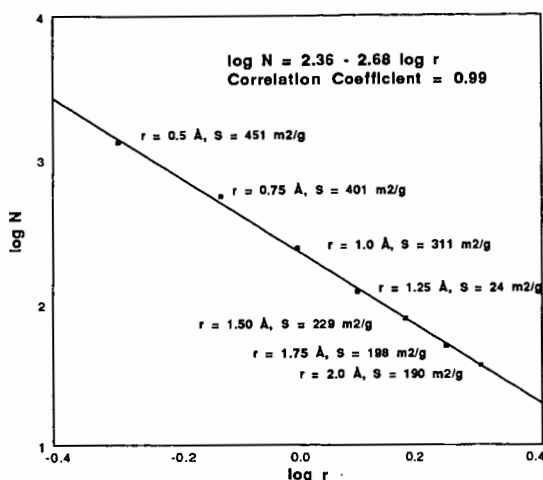


Fig. 2. Effect of the cell grid size on the micropore surface areas for the first model of the sample ( $C_{333}H_{302}O_{14}$ ).  $N$  is the number of cell faces which belong to the surface of micropore volume,  $r$  is the size of the cells used in the surface area calculations (cf METHOD). The fractal dimension ( $D$ ) is defined by the following equation:  $N \propto r^{-D}$  or  $\log N \propto -D \log r$

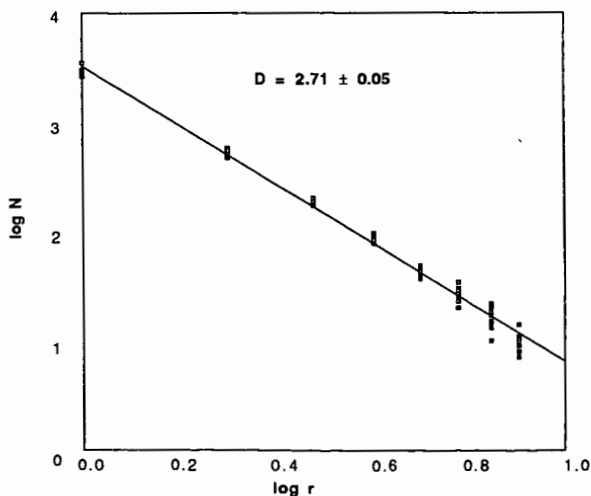


Fig. 3. Fractal dimension of the total surface area for the 15 models comprising the sample.  $N$  is the number of cell faces which belong to the surface of the models,  $r$  is the size of the cells used in the surface area calculations (cf METHOD).